



STUDY ON SELECTED NATURAL PLANT SUBSTRATE AND PROTEIN RESIDUE FOR ABSORBENT APPLICATION IN HYGIENE PRODUCTS

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ABSTRACT

Absorbent polymers are commonly made from petrochemical starting materials, i.e., acrylic monomers. Special hydrogels as superabsorbent materials are widely employed in hygienic uses particularly disposable diapers and female napkins where they can capture secreted fluids, e.g., urine, blood, etc. Agricultural grade of such hydrogels are used as granules for holding soil moisture in arid areas. The biopolymer-contained Absorbent polymers, however, possess typically higher cost and less performance than their fully synthetic counterparts. Absorbent polymers have created a very attractive area in the viewpoint of super-swelling behaviour, chemistry, and designing the variety of final applications. When working in this field, we always deal with water, aqueous media and bio-related systems. Thus, we increasingly walk in a green area becoming greener via replacing the synthetics with the bio-based materials, e.g., polysaccharides and polypeptides. This, however, is a long-term perspective. More or less, the acrylic kingdom will extend its domination in the future markets. The present article represents a different outlook; it gives an account of all types of SAP materials with a practical viewpoint from structure to usage, based on either the current literature or our long experience on these materials. The main target is appraisal the Absorbent polymers to be useful for either academics or industries.

Keywords: hygienic product, bio based material, SAP materials, Absorbent polymers.

INTRODUCTION

Among natural materials, water soluble polysaccharides and polypeptides are becoming the primary sources of sericin. Starches, water soluble celluloses, and polygalactomans, such as sweet potato starch, potato starch, wheat starch, maize starch, rice starch, and tapioca starch, are common sources. The majority of the qualities of natural gums (arabic, guar, gellan, ghatti, karaya, kondagogu, konjac, locust bean tamarind, tragacanth, tara, and xanthan) are comparable to sericin. They have the ability to absorb and hold moisture through swelling. Natural polymers

like cotton, rayon, and wood pulp are naturally absorbent. Chemical treatment can make these fibres superabsorbent. Sugar palm fibre, kenaf, bamboo, and banana can all be blended together to make sericin. This will improve their mechanical and chemical qualities, which are necessary for sericin to function.[4] Sericin is known for having the maximum fluid absorption in a saline media. The sericin's rate of absorption can be calculated based on its use. sericin has the maximum absorbency under load, the longest lasting and stable swelling even during storage, and the least soluble content and residual monomer. Another significant feature of sericin is its rewetting ability, which means it should not leak fluid after absorption even when a load is applied. The sericin does not need to have all of the features mentioned above. It should have the properties necessary for its intended usage at a high level of optimization. For example, the highest absorbency and lowest rewetting, or even no rewetting, are the most important features to have in hygiene products.[10]

The ability to absorb menstrual fluid is the most important feature of a sanitary pad. As a result, the absorbency and retention properties of the core fibre determine its selection. Scouring and bleaching increase the absorbency of natural fabrics. Hydrogel made of cellulose boosts absorbency even more. Because natural fibre contains no synthetic components, it is the greatest material for generating absorbent for feminine hygiene products. The basic criterion for a good absorbent in a feminine hygiene product should be natural pH balances that do not cause irritation or yeast infection (Cannabis Cosmetics, 2012). When a highly compressed fibre is absorbed, it expands, and when a weakly compressed fibre is absorbed, it collapses. To retain the structural integrity of absorbent material, compression is essential. However, bio-modified or natural-based Absorbent polymers are being interested due to the world steadfast decision towards the environmental protection. Besides various applications, the most volume of SAP world production (10 6 tons/year) is yet consumed in hygienic uses, i.e., disposable diapers (as baby or adult diapers, feminine napkins, etc.). Meanwhile, a very beneficial section related to the practical methods of the SAP testing and evaluation has also been included in the analytical evaluation section.

Sericin is a protein created by *Bombyxmori* (silkworms) in the production of silk. Silk emitted by the silkworm consists mainly of two proteins, sericin and fibroin; fibroin being the structural center of the silk, and sericin being the gum coating the fibres and allowing them to stick to each other. Silk sericin has been used for over 3500 years by the world elite to rejuvenate their hair and skin. The chemical composition of sericin is $C_{30}H_{40}N_{10}O_{16}$. Silk sericin due to its proteinous nature is susceptible to the action of proteolytic enzymes present in body and hence it is digestible. This property makes it a biocompatible and biodegradable material. Because of some additional properties like, gelling ability, moisture retention capacity, and skin adhesion. it has wide applications in medical, pharmaceutical, and cosmetics. Sericin, a major component of silk, has a long history of being discarded as a waste during silk processing. The value of sericin for tissue engineering is underestimated and its potential application in regenerative medicine has just begun to be explored. Here we report the successful fabrication and characterization of a covalently-cross linked 3D pure sericin hydrogel for delivery of cells and drugs. This hydrogel is injectable, permitting its implantation through minimally invasive approaches. Notably, this hydrogel is found to exhibit photoluminescence, enabling bio-imaging and in vivo tracking. Moreover, this hydrogel system possesses excellent cell-adhesive capability, effectively promoting cell attachment,

proliferation and long-term survival of various types of cells. Further, the sericin hydrogel releases bioactive reagents in a sustained manner. Additionally, this hydrogel demonstrates good elasticity, high porosity, and pH-dependent degradation dynamics, which are advantageous for this sericin hydrogel to serve as a delivery vehicle for cells and therapeutic drugs. With all these unique features, it is expected that this sericin hydrogel will have wide utility in the areas of tissue engineering and regenerative medicine.

Cross linking Agents and Initiators

Citric acid

Citric acid is an organic tricarboxylic acid that can be found in most fruits, especially lemons and oranges. Because it's utilised as a preservative, it's non-toxic and has a wide range of applications in the food industry as a safe natural addition. This acid has the ability to crosslink hydroxyl groups in polyose and has been observed at high temperatures (165-177 °C). In some doses, acid can even behave as a plasticizer.[21]

Boric acid

Boric acid, also known as hydrogen borate, boracic acid, and orthoboric acid, is a boron Lewis acid that is weak and monobasic. However, its behaviour toward certain chemical reactions suggests that it is acid in the Bronsted sense as well. Boracic acid is frequently employed as an antiseptic, insecticide, flame retardant, nucleon absorbent substance, or a precursor to other chemical compounds. Boric acid, a non-toxic substance, is thought of as a Lewis acid (electron acceptor) with an empty p orbital that might be used to form groups within polyvinyl resin molecules to achieve chemical cross-linking.

Methylene bisacrylamide

In electrophoresis gels, bis-acrylamide is used to establish crosslinks between acrylamide to produce polyacrylamide gels. The porosity properties of the polyacrylamide gel are controlled by the ratio of bis-acrylamide to acrylamide. The NNMBA-cross links with their hydrophilic/hydrophobic balance and lower rigidity impart moderate swelling in water[22]

Potassium persulfate

Potassium Persulfate is a sand-like substance that is colorless or white and odourless. It's used to make soap and colors, as well as in photography and medicine. Acrylics, polyvinyl chlorides, polystyrenes, and neoprene are all made with persulfates as initiators for emulsion polymerization processes. They are employed in the production of synthetic rubber (styrene butadiene and isoprene) for automobile and truck tyres as polymerization initiators.[4]

Carboxymethyl cellulose

Carboxymethyl cellulose, often known as cellulose gum, is a cellulose derivative that contains carboxymethyl groups attached to some of the hydroxyl groups of the glucopyranose monomers that make up the cellulose backbone. Its sodium salt, sodium carboxymethyl cellulose, is frequently utilised. The alkali-catalysed reaction of cellulose with chloroacetic acid produces carboxymethyl cellulose.[20]

Materials

The initial natural products which were used for trials of hydrogel are natural resins like Drumstick resin, Mesquite resin, Almond resin, and natural seeds like chia seeds, basil seeds, Sericin seeds. All of these chosen products have

polysaccharide content which has many OH groups which will help in bonding with water molecules and holds them in place. The crosslinking agent used boric acid and citric acid, N,N'-methylenebisacrylamide (MBA), potassium persulphate, NaOH, sodium alginate.

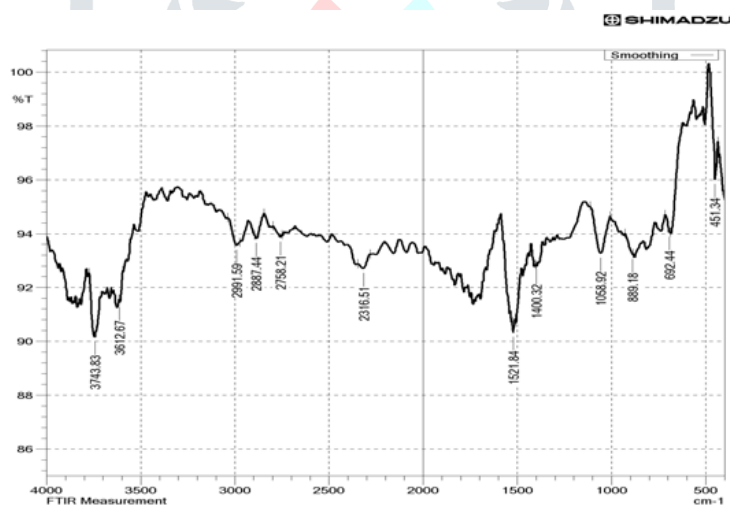
Method

Initially the absorption of procured natural products has to be determined by tea bag test method for selection of suitable materials in order to proceed for sericin // natural resin preparation.

Fourier transform infrared spectral analysis (FTIR)

Fourier transform infrared (FTIR) spectroscopy is used to identify different organic functional groups present in natural substances. Fourier transform infrared spectroscopy (FT-IR) spectra of almond resin samples were recorded on an FTIR Spectrophotometer at room temperature. The almond resin and Sericin gel powder samples were mixed with potassium bromide powder (KBr) and made into pellets before measurement.

The main purpose of this analysis was to identify the functional groups of the substrate. The spectra are recorded using a spectrometer, equipped with an attenuated total reflectance (ATR) module with a diamond crystal and driven by the Opus/Mentor software. The substrate was dried at 50°C for 24 hours and then powdered to the size of 315 µm. A few milligrams of powder from the substrate studied were deposited on the diamond crystal of the ATR module. Acquisitions were carried out by scanning over a spectral region ranging from 4000 to 400 cm⁻¹



with a resolution of 4 cm⁻¹.

Fig. FTIR Image of Moringa powder

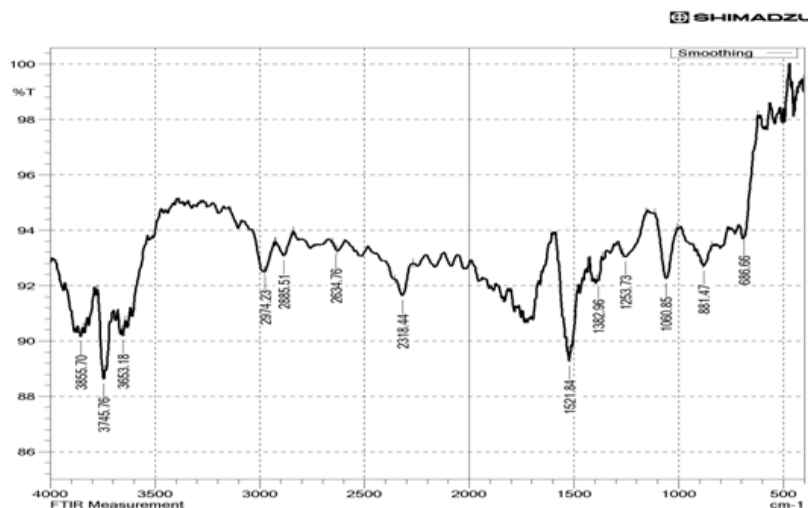


Fig. FTIR Image of Almond powder

Standardization of instrument was carried out using potassium bromide powder (KBr) pellet as blank and the spectra were recorded in the range of 400–4000 cm^{-1} . In almond resin, the spectral bands falling between 3000–3600 cm^{-1} and 2800–3000 cm^{-1} correspond to O H and C H stretching modes respectively. Peaks observed at 3523.95 cm^{-1} in the spectra are therefore due to the presence of O H groups.

The major IR-bands at 2910.87 cm^{-1} observed for almond resin were assigned to the vibrational modes of C H group. . Peaks present in the spectra at 1625.9 cm^{-1} , 1627.9 cm^{-1} and 1436.91 cm^{-1} correspond to the presence of COOH (carboxylic group). Carboxylic acids show characteristic O H in-plane bending band at 1431 cm^{-1} . Peaks centered at 1436.9 cm^{-1} and 1438.9 cm^{-1} wavenumbers may be due to the symmetrical stretching of carboxylic groups of uronic acid residues of gum polysaccharides. The peaks observed between 800 cm^{-1} and 1201 cm^{-1} represented C O, C C & C O C stretching, and C O H, C H bending modes of the polymer backbone. Bands identified in the spectra at 723.3 cm^{-1} may be assigned to 1–4 linkage of galactose. FT-IR bands centered at 1072.32 cm^{-1} in the spectrum of almond resin may correspond to the presence of galactan. In Sericin gel powder, a broad and strong peak observed at 3,400 cm^{-1} demonstrated the presence of stretching vibration of the hydroxyl group (OH) forming the hydrogen bonds with each other. The existence of a weak stretching vibration at 2,933.7 cm^{-1} was due to the presence of saturated bonds of C–H (symmetric and asymmetric of the free sugar). The C=O asymmetric stretching vibration at 1,610 cm^{-1} was attributed to the carboxyl group indicating the presence of uronic acids or bound water in Sericin gel powder. The carboxyl group acts as a binding site for ions, hence has a great influence on gelling and rheological properties. The absorption at 1,415 cm^{-1} was referred to C–O stretching vibration and revealed the existence of uronic acids. The area between 800 and 1,200 cm^{-1} is recognized as the fingerprint region for carbohydrates that can be used as a good indicator to assess the structural differences in various gums.

Furthermore, the peak at 1,145 cm^{-1} recommended the existence of the glycosidic linkages Y C–O–C and C–OH. The diagnostic peaks at 1,072 and 1,041 cm^{-1} as- certain the presence of guluronic acid, mannuronic acid, and O-acetyl ester. The absorption at 1,041 cm^{-1} indicated the presence of glucan units or referred to the C–O stretching vibration in the pyranose ring. The band at 1,072 cm^{-1} indicated the presence of mannose in Sericin gel powder. The bands in the range of 810–839 cm^{-1} were assigned to α -d-Galactose. Absorption peaks at 534 and 628 cm^{-1} is due

to polymer backbone bending and attributed to triply deteriorated bending modes of the O–P–O bond vibrations in the phosphate groups.

EDX Analysis

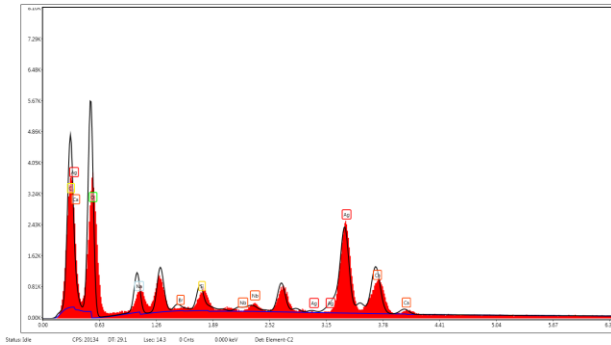


Fig . EDX image of moringa powder

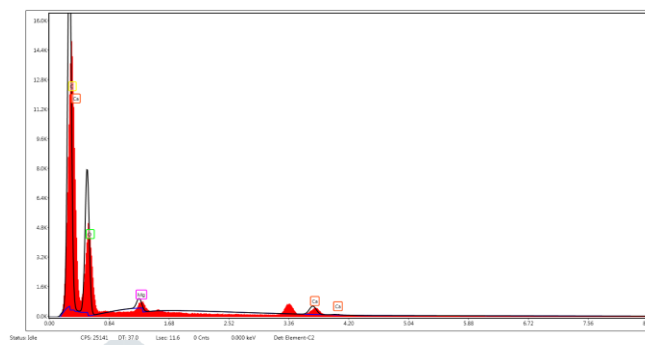


Fig . EDX image of almond resin

The EDX analysis (energy-dispersive X-ray analysis), referred to as EDS or EDX, is an X-ray technique used to identify the elemental composition of materials. The data generated by EDX analysis consist of spectra showing peaks that correspond to the elements making up the true composition of the sample being analyzed. Elemental mapping of a sample and image analysis are also possible. The technique can be qualitative, semi-quantitative, and quantitative and also provide the spatial distribution of elements through mapping. In Sericin gel powder has carbon, sodium, oxygen, calcium in K shell and bromine, rhodium, silicon, silver in L shell. In almond powder has potassium, magnesium, carbon, oxygen, calcium in K shell.

Test for Sericin / natural resin

Tea bag test method refers to the amount (g) of standard fluids absorbed per gram of the resins. The teabags were filled with 0.5 g of sericin / natural resin sample, distributed equally through the teabag, immersed in water for 60 mins, after 60 mins, removed from the water and left for 10 min to drain off the excess solution, then weighed.

Hydrogel preparation from various natural resins:

Hydrogel was prepared using various natural resins with different combination of cross linking agents and initiators. The prepared hydrogel was then dried and powdered for absorbency test.

Table.1 Hydrogel preparation from various natural resins

Trail no	Material 1	Material 2	Cross linking agent	Initiator	Distilled water
1	Moringa resin(1g)	Sericin	0.5 g of boric acid	–	30 ml
2	Mesquite resin(1g)	Sericin	0.5 g of boric acid	–	30 ml
3	Almond	Sericin	0.5 g of boric acid	–	100ml

	resin(1g)		acid		
4	Almond resin(2g)	Sericin / Moringa resin(1g)	0.5 g of boric acid	–	100 ml
5	Almond resin(1g)	Sericin / Mesquite resin (1g)	0.5 g of boric acid	–	100 ml

Hydrogel Preparation from Moringa

Hydrogel extraction process was carried out for chia seeds, basil seeds and moringa seed. As chia seed and basil seed does not form hydrogel, moringa seed alone was taken for further process.

Preparation of Gel Powder

Boil moringa seed at 90 degree Celsius and stir it the Sericinseed for a few minutes. Reduce heat to medium-low until it achieves gel consistency. And separate the moringa seed and gel by filtration. Allow it to cool.

Tea bag test for absorbency (US patent 5419955):

1.0 g of super absorbent material was weighed and recorded as W_1 to be taken into the tea bag and sealed. An empty teabag was also prepared to act as the blank. A beaker was filled with distilled water solution up to 4 cm depth and a beaker is filled with formula milk solution at room temperature. The particles of hydrogel powder were distributed uniformly throughout the tea bag. Teabags with hydrogel powder and without hydrogel powder were held horizontally and laid on the surface of the solution to wet the surface of teabags for 1 min before they were submerged into the solution. After soaking for 60 min., the teabags were removed from the solution and allowed to drip excess solution for 15 min. The weight of teabag with hydrogel powder was weighed and recorded as W_3 . Empty teabag was also weighed and recorded as W_2 . The absorbing capacity was calculated using the Equation,

$$\text{Absorbency capacity} = (W_3 - W_2) - W_1 / W_1$$

Absorbency under load

Absorbency under load can be a measurement of the swollen gel stability and swollen gel strength of superabsorbent. 0.9g of hydrogel powder was measured and recorded as W_1 and scattered evenly inside a teabag. The teabag was put horizontally into a hollow steel cylinder. The steel cylinder along with the teabag was put onto a beaker. A set of 3 cylindrical solid weights with 1.0 g of weight each solid, which can slip freely into the steel cylinder were used as the static load to apply pressure of 0.3, 0.6, and 0.9 psi respectively. Then 10 ml of saline solution and formula milk solution was poured into the hollow steel cylinder. After 1 h, the teabag was removed from the steel cylinder, and the weight was measured and recorded as W_2 . Absorbency under load was calculated by using the Equation

$$\text{Absorbency under load (g/g)} = (W_2 - W_1) / W_1.$$

Rewetting under load

Re-wet value is very important to be tested to ensure the swollen super absorbent can retain the liquid to prevent the liquid from leaking back to the surface. A filter paper with 11 cm diameter was tore into four even parts. The weight of a stack of 24 pieces of the tore filter paper were measured and recorded as W_1 . 0.5 g of hydrogel powder was measured and recorded as W_1 and scattered evenly inside a teabag. The teabag was put horizontally into a hollow steel cylinder. The steel cylinder along with the teabag was put onto a beaker. A set of 3 cylindrical solid weights with 1.0 g of weight each solid, which can slip freely into the steel cylinder were used as the static load to apply pressure of 0.3, 0.6, and 0.9 psi respectively. Then 10 ml of distilled water solution / milk was poured into the hollow steel cylinder. After 10 mins the tea bag is removed and the stack of filter paper is placed over. After 2 mins the stack of filter was weighed and recorded as W_2 . Rewetting under load was calculated using the Equation,

$$\text{Rewetting under load (g)} = W_2 - W_1.$$

Tea bag test for absorbency

Table.2 Tea bag test for absorbency

In tea bag test method, Sericin absorbency nearly equal to commercially available SAP

SAMPLE	Saline solution (g)	Protein Solution (g)
Almond	5.1	6.8
Moringa	9.6	9.9
Almond & sericin / Moringa (50:50)	8.7	5.5
Almond & sericin / Moringa (70:30)	6.6	4.6
Almond & sericin / Moringa (30:70)	8.8	7.0

Absorbency under load**Table 3. Absorbency under load for resins and seeds**

SAMPLE	Saline solution(g)	Protein solution(g)
Almond	5.7	5
Moringa	5	4
Almond & sericin / Moringa (50:50)	6	4.7
Almond & sericin / Moringa (70:30)	5.7	4.5
Almond & sericin / Moringa (30:70)	4.5	4.8

Milk solution showed highest absorbency for Almond whereas saline and blood solution are absorbed the highest FOR Sericin/almond (50:50) thus comparable with the commercial available SAP. The most volume of SAP produced all over the world is used in disposable diapers. Therefore, most research works have been focused on hygienic grades which are usually used with fluff in diapers. Proteins can also be modified by either polysaccharides or synthetics to produce hybrid hydrogels with super-swelling properties. For instance, the researchers have studied the water swelling property of binary polymer networks (frequently as interpenetrated polymer networks, IPNs) of modified proteins with some water-soluble, hydrophilic, biodegradable, and non-toxic polymers, e.g., modified soy protein, gelatin, sodium carboxymethyl cellulose (CMC), poly(ethylene glycol) (PEG), poly(vinyl alcohol), guar gum, chitosan, and carboxymethyl chitosan. Although the majority of the super absorbents are nowadays manufactured from synthetic polymers (essentially acrylics) due to their superior price-to efficiency balance, the worlds firm decision for environmental protection potentially support the ideas of partially/totally replacing the synthetics by "greener" alternatives. Carbohydrate polymers (polysaccharides) are the cheapest and most abundant, available, and renewable organic materials. Chitin, cellulose, starch, and natural gums (such as xanthan, guar and alginates) are some of the most important polysaccharides.

Rewetting under load**Table.4. Rewetting under load**

Sample	Saline solution(g)	Protein solution(g)
Almond	0.98	0.99
Moringa	0.8	0.98
Almond & sericin / Moringa (50:50)	1.6	1.2
Almond & sericin / Moringa (70:30)	1.3	1.4
Almond & sericin / Moringa (30:70)	1.1	1.3

In rewetting under load test, Sericin shows the lowest rewetting capacity for protein and saline solution and Almond & sericin / Moringa (70:30) for blood solution thus comparable with the commercial available SAP. Absorbent polymers as hydrogels, relative to their own mass can absorb and retain extraordinary large amounts of water or aqueous solution. These ultrahigh absorbing materials can imbibe deionized water as high as 1,000-100,000% (10-1000 g/g) whereas the absorption capacity of common hydrogels is not more than 100% (1 g/g). In fact, the synthetic components for achieving the maximum level of some of these features will lead to inefficiency of the rest. Therefore, in practice, the production reaction variables must be optimized such that an appropriate balance between the properties is achieved.

Conclusion

Special hydrogels are superabsorbent material are widely employed in hygienic used particularly disposable diaper and female napkins where they can capture secreted fluids, e.g., urine, blood, etc. agriculture grade of such hydrogels are used as granules for holding soil moisture in arid areas. The hygroscopic material usually categorized into two main class based on the major mechanism of water absorption, i.e., chemical and physical absorptions. Chemical absorbers (e.g., metal hydrides) catch water via chemical reaction converting their nature. Physical absorbers imbibe water via four main mechanism; reversible changes of their crystal structure(e.g., silica gel and anhydrous inorganic salts); physical entrapment of water via capillary forces in their macro-porous structures(e.g., soft polyurethane sponge); a combination of the mechanism (ii) and hydration of functional group (e.g., tissues paper); the mechanism which maybe anticipated by combination of mechanism of (ii) and (iii) and essentially dissolution and thermodynamically favored expansion of the macro- molecular chain limited by cross-linkages. The unique attributes of superabsorbent polymer make them useful in many different application. The liquid absorption and retention ability makes them useful in disposable hygienic products. They include infant diapers, feminine hygiene pads, and adult's incontinence products. Other absorbent products suitable for superabsorbent polymers are paper towels, surgical sponges, meat trays, disposable mats for outside doorways, household pet litter, bandage, and wound dressings.

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